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ABSTRACT

Three different models which use the Monte Carlo method have been developed to predict the molecular weight, composition, and hard segment length distribution of polyurethane block copolymers polymerized under varying conditions. The simplest model tries to describe natural compositional heterogeneity that arises in polyurethanes due to the nature of the polymerization even under ideal conditions. The subsequent models introduce nonidealities into the simulation that actually occur in real polymerizations, including premature phase separation of the reactants and unequal reactivities of the monomer species. In this investigation, these models are used to simulate experimental data reported by MacKnight and coworkers on polybutadiene polyurethanes. The results of the modelling strongly support the hypothesis of MacKnight and coworkers that phase separation occurred near the beginning of the polymerization. The primary effect of the phase separation is to limit the degree of polymerization (molecular weight) in each phase presumably due to stoichiometric imbalances of reactants resulting from an unequal partitioning of the reactants in the two phases. The low molecular weights, in turn, lead to a broad composition distribution. The broad molecular weight distribution results from having a different average degree of polymerization in each phase, although allophonate cross-linking may also be a contributing factor. Differences between the three models and their utility for simulating experimental data are also discussed.

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Monte Carlo Simulation Study of the Polymerization of Polyurethane
Block Copolymers. IV. Modelling of Experimental Data

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ABSTRACT

Three different models which use the Monte Carlo method have been developed to predict the molecular weight, composition, and hard segment length distribution of polyurethane block copolymers polymerized under varying conditions. The simplest model tries to describe natural compositional heterogeneity that arises in polyurethanes due to the nature of the polymerization even under ideal conditions. The subsequent models introduce nonidealities into the simulation that actually occur in real polymerizations, including premature phase separation of the reactants and unequal reactivities of the monomer species. In this investigation, these models are used to simulate experimental data reported by MacKnight and coworkers on polybutadiene polyurethanes. The results of the modelling strongly support the hypothesis of MacKnight and coworkers that phase separation occurred near the beginning of the polymerization. The primary effect of the phase separation is to limit the degree of polymerization (molecular weight) in each phase presumably due to stoichiometric imbalances of reactants resulting from an unequal partitioning of the reactants in the two phases. The low molecular weights, in turn, lead to a broad composition distribution. The broad molecular weight distribution results from having a different average degree of polymerization in each phase, although allophanate cross-linking may also be a contributing factor. Differences between the three models and their utility for simulating experimental data are also discussed.

Introduction

Polyurethane block copolymers can be polymerized under a wide variety of conditions leading to different molecular weight, hard segment length and composition distributions¹⁻⁶. The effects of changing these distributions on the morphology and properties of polyurethane block copolymers has generally received little attention although several studies have been reported describing the effects of varying one of the distributions⁷⁻¹³. Three major factors have inhibited progress towards gaining a better understanding of the effects of these distributions on sample properties and morphology. First, many investigators have ignored or neglected effects of this type without even attempting to gather experimental data for the distributions in their materials. It is likely that in many cases the effects due to varying these distributions are small especially in comparison to other varied parameters, yet without at least some experimental characterization assuming the effects to be negligible may lead to erroneous conclusions concerning structure-property relationships. Second, it is difficult to obtain meaningful experimental data on the molecular weight, composition and hard segment length distributions of polyurethane block copolymers. Information of this type is difficult to obtain for copolymers in general^{14,15} and is even more difficult to obtain for polyurethanes because of their solubility characteristics, the many potential species that can be produced due to side reactions such as allophanate crosslinking, and the fact that they are actually formed from three and not two different monomers^{1,16}. This difficulty of characterization has, no doubt, fostered the neglect of effects of the type noted above. Finally, the complexity of the polyurethane polymerization reaction has hindered the development of a direct theoretical approach towards predicting the various distributions under given polymerization conditions. Peebles^{5,6} has shown that under certain ideal conditions the hard segment length distribution should follow a most probable distribution. Case¹⁷ has derived equations describing the molecular weight distribution, but except

for the calculation of \bar{M}_n the equations are rather unwieldy. Lopez-Serrano et al.¹⁸ have developed a method using a recursive technique that can be used to calculate averages of the various distributions.

One approach to overcoming some of the difficulties noted above is to use special synthetic techniques to produce simplified systems, for example, materials with approximately monodisperse hard segment length distributions^{12,13}. Materials of this type are valuable in two respects. First, since the hard segment length is well defined its effects on sample morphology and properties can be more directly elucidated. Second, the ability to control the hard segment length distribution could be used to hold it constant while varying other parameters such as molecular weight.

An alternate approach is to develop models of the polymerization process that can be used to predict the composition, molecular weight and hard segment length distributions of polyurethane block copolymers polymerized under various conditions. Models of this type are of interest for two reasons. First, they can be used to simulate the effects of varying polymerization parameters on the various distributions. Second, it is possible by using models and a limited amount of experimental data to predict the entire composition, molecular weight and hard segment length distributions. These calculated distributions could then be used along with experimental morphology and property data to investigate the effects of varying the distributions. The predicted distributions are, of course, only as good as the model and the assumptions therein and the quality of the experimental data. Furthermore, it is likely that many distributions can be simulated that produce the known experimental parameters. Obviously, the acquisition of more and better experimental data would allow for increased distinction between various models, more accurate values of model parameters and/or increased model complexity.

In the first three contributions in this series¹⁻³, three different models were developed and described that use Monte Carlo methods to predict the molecular weight, composition, and hard segment length characteristics of polyurethane block copolymers polymerized under various conditions. The models differ in the assumptions made about the polymerization process leading to the use of different parameters to describe various polymerization effects. Therefore, as discussed previously, a particular model may be more suited to describing a particular type of reaction, such as a one or two-step polymerization¹⁻³. Although the three different models: the single-phase ideal reaction model¹, the two-phase ideal reaction model², and the simple sinking pool model³, will be described briefly here; for more detailed information the reader is referred to the references cited above.

In the previous contribution the effects of varying model parameters on the predicted distributions were investigated; however, actual experimental data were not modeled. The purposes of this investigation were (1) to demonstrate how the various models can be used to simulate experimental data, (2) to determine for a given material which model provides the 'best fit' and (3) to draw any conclusions or insights regarding the utility of the models and the structure-property relationships of the actual materials based on the results of (1) and (2). Therefore, in this contribution the three models described previously¹⁻³ will be used to simulate data on polybutadiene polyurethanes reported by MacKnight and coworkers^{18,19}. These materials which are described below were chosen for study for several reasons. First, experimental molecular weight and composition information was already available^{19,22}. Second, these materials were thought to have undergone phase separation during polymerization due to the incompatibility of the reactants leading to unusual molecular weight and composition distributions and thus were good candidates for modelling by the two-phase ideal reaction and simple sinking pool models. Finally, the results

of this investigation and the previous investigations by MacKnight and coworkers demonstrate the large effects on morphology and properties that can be associated with large changes in the composition, molecular weight and hard segment length distributions. However, it should be noted that it was not the objective of this investigation to determine the effects of varying a particular distribution on the sample properties or morphology. The various models and the materials to be modelled are described briefly below.

Description of Materials

The synthesis and characterization of the polybutadiene based polyurethane block copolymers has been reported by MacKnight and coworkers^{19,22}. The samples were prepared using a two-step bulk reaction by reacting a hydroxy-terminated PBD oligomer ($\bar{P}_n = 1.97$, $\bar{M}_n = 2200$ and $\bar{M}_w/\bar{M}_n = 1.5$) with an isomeric blend of toluene diisocyanate (TDI) followed by chain extension with butanediol²³. The product materials exhibited two hard segment glass transition temperatures, low molecular weight and poor mechanical properties. Xu et al.¹⁸ fractionated the samples into sol and gel fractions in N,N-dimethylformamide (DMF) at 70°C. They studied the composition and thermal characteristics of the resulting fractions by infrared spectroscopy (IR) and differential scanning calorimetry (DSC). The IR results indicated that the sol fraction had a much higher hard segment content than the gel fraction. In effect, the sample could be thought of as a blend of two polyurethanes with different stoichiometries. For example, a blend of a material with a 10/9/1 molar ratio of isocyanate to chain extender to polyol with a 2/1/1 molar ratio material will produce a nominal 6/5/1 material with a bimodal hard segment distribution and broad composition distributions.

MacKnight and coworkers observed that when butane diol was added in the second step of the reaction it formed a separate phase immediately. This behavior was observed for both crystallizable and non-crystallizable hard segments

indicating that the cause of the phase separation was not crystallization but the incompatibility of the reactants. A scenario for the polymerization was suggested where the isocyanate diffused into butane diol droplets and reacted to produce regions of virtually pure hard segment polymer. The isocyanate capped soft segments could not readily diffuse into the butane diol droplets and thus reacted primarily at the boundary between the two phases or by diffusion of butanediol into the soft segment-rich phase. The final morphology of the polymer was largely determined by this phase separation during polymerization. The DSC results of Xu et al.¹⁸ showed that the sol and gel fractions exhibited different hard segment glass transition temperatures that corresponded to the two T_g 's observed in the unfractionated material. These transitions were attributed to long hard segments in the hard segment-rich phase and short hard segments in the soft segment-rich phase, respectively.

Xu et al. attributed the poor mechanical properties of these materials to the brittle behavior of the hard segment rich material and to low overall molecular weight caused by an imbalance in isocyanate and hydroxyl groups in the individual phases of the reaction mixture. Subsequent work on PBD polyurethanes synthesized in solution to reduce reactant incompatibility effects²² led to higher molecular weights and improved physical properties. No evidence for compositional heterogeneity was observed in these samples in that two hard segments T_g 's were not observed and it was noted that samples could not be fractionated in DMF²². Finally, Xu et al. suggested that reactant incompatibility effects leading to compositional heterogeneity should be common in polyurethanes, but were especially evident in this system because of the large polarity difference of the reactants.

Model Description

The first and simplest model is the so-called single phase ideal reaction model (SPI)¹. This model is based on the assumptions of Peebles^{5,6}, notably

equal reactivity of chain extender and polyol and no effects of molecular weight (chain length) on reactivity, that lead to a most probable distribution of hard segment lengths at 100% conversion. The other major assumption is that the degree of polymerization (D_p) in terms of hard and soft segments follows the most probable distribution. Also, the model assumes stoichiometric conditions. Prior to the building up of any chains, three large arrays representing the degree of polymerization distribution, hard segment length distribution, and soft segment length or molecular weight distribution are created based on the values of various selected parameters such as the stoichiometry, average D_p , etc. The soft segment molecular weight distribution is based on experimental data or a Schulz distribution with a known \bar{M}_w/\bar{M}_n value can be used. The Monte Carlo methodology is then implemented as follows. First, a D_p is selected at random and a random assignment of either beginning with a hard or soft segment is made. Hard and soft segments are then alternately selected at random and added to the growing chain until the selected D_p value is reached. The process is then repeated for the next chain continuing until typically 15000 chains have been created.

The various distributions can then be calculated and a simulated fractionation can be carried out. In the fractionation procedure, the weight fraction of chains starting with the lowest hard segment content chains is summed up to a specified weight fraction. The fractionation thus takes place solely on the basis of composition. The average molecular weight and composition for that fraction and the remaining fraction are then calculated. This data can then be compared to experimental fractionation data of the type reported by Xu et al.¹⁹.

The second model, the two-phase ideal reaction model (TPI)², is a modified version of the SPI. The difference is that before building up any chains the monomer species are partitioned into two separate phases, one that is rich in

the polyol species and one that is rich in the diol species. The fraction of polyol in the polyol rich phase along with the fraction of diisocyanate in the hard segment-rich phase can be selected. The model then divides the chain extender so that the reaction mixture in each phase is stoichiometric. After the monomers are divided between the two phases, the average degree of polymerization is chosen for each phase, since there is no reason to believe that the degree of polymerization of each phase will be identical²⁴. The building up of chains in the two phases is then done in the same manner as described for the single-phase ideal reaction model. Finally, before the simulation of fractionation or calculation of the various distributions the products of the two phases are recombined.

The third model, the simple sinking pool model (SSP) is fundamentally different than the other two models. In the previous models the chains were built up sequentially by whole soft or hard segments from what amounted to an infinite pool. In this model, the pool of monomers is finite and the chains are polymerized simultaneously so that the simulation more accurately reflects the actual polymerization conditions. The probability of a given species being the next to react is not constant, as it was in the single-phase ideal reaction model, but depends on the number of that type of monomer remaining in the pool. There are other advantages to this method. The hard segment sequence length distribution is not calculated using the equations of Peebles^{5,6} as was done in the single-phase ideal reaction model. The effect of finite molecular weight on the hard segment sequence length distribution can then be examined. Also, the sinking pool model represents the actual distribution of the total degree of polymerization of the chain better than the single-phase ideal reaction model, which defined a whole segment as a monomer unit rather than using the real monomer units. Finally, the model can treat cases with excess isocyanate (non-stoichiometric) but does not include any effects due to cross-linking.

The SSP also allows simulation of two other effects, self-affinity and unequal reactivity of the chain extender and the polyol. The self-affinity effect is used as a method of simulating phase separation during polymerization. In the model a growing chain has a memory of which diol (chain extender or polyol) species have recently been added to the chain and the probability of reacting with the next diol is influenced by the previously reacted diols. The concept behind this is that chains that have recently reacted with a large number of chain extenders are more likely to be near a chain-extender-rich phase than near a polyol-rich phase. They will therefore be more likely to react with a diisocyanate followed by another chain extender than with a diisocyanate followed by a polyol. In the model, the self-affinity factor (SAF) determines the magnitude of the self-affinity effect while a second parameter (NSA) determines the D_p value for a given chain at which self-affinity effects start to be calculated.

Nonequal reactivity of the diol species is handled in a similar fashion. The probability of reacting with a chain extender is multiplied by the reaction competitiveness factor (RCF) which can be greater or less than one depending on whether the chain extender is thought to be more or less reactive than the polyol. Both the self-affinity and unequal reactivity effects can cause depletion of one of the monomers, however at that point the probability of reacting with the depleted monomer type goes to zero since as noted above the probability of reaction also depends on the number of monomers in the pool.

The three models were designed for different polymerization conditions and purposes. The single-phase ideal model was designed to simulate one or two step solution polymerizations where the assumptions made by Peebles are most likely to be valid. Also, as shown in the next section the model is useful as a sort of negative test to determine whether non-ideal effects have occurred. The two

non-ideal models (TPI and SSP) are both designed to simulate phase separation during polymerization but have some noticeable differences. The two-phase ideal reaction model should be best suited for systems where phase separation occurs very early in the reaction while the sinking pool method can simulate phase separation at various points by changing the value of the NSA parameter. Also as noted above the D_p 's are defined differently with the result that the sinking pool method should be more accurate at very low degrees of polymerization. Additionally the sinking pool model allows for unequal reactivities of the chain extender and polyol but unlike the TPI model does not incorporate the diisocyanate reactivity ratio (μ) and is thus better suited for one-step reaction. Other differences between the models will become apparent in the next section.

Results and Discussion

Table 1 contains a summary of the experimental composition and molecular weight data for the polybutadiene polyurethane samples reported previously^{19,21}. The first column in Table 1 identifies the sample using the following nomenclature. The first part of the nomenclature (4T4, 4T10 or 6T4) identifies whether the sample is based on 2, 4 (4T) or 2, 6 (6T) TDI while the following 4 or 10 represents the approximate molar ratio of the isocyanate to the polybutadiene polyol. The middle part of the nomenclature, for example 4.2/3/1 is the ratio of the isocyanate to the chain extender (butane diol) to the PBD polyol used in the synthesis. The final number, for example 31.3, is the calculated hard segment content (isocyanate plus chain extender) based on the amounts added in the synthesis and a \bar{M}_n for the PBD soft segments of 2200 ($\bar{M}_w/\bar{M}_n = 1.5$).

The second and third columns in Table 1 contain the weight fraction values for the portions of the sample that were found to be soluble or insoluble in DMF at 70°C¹⁹. The compositions of the soluble and insoluble fractions as determined by infrared spectroscopy (IR) are listed in columns 4 and 5 and the overall compositions calculated from these data and the weight fraction values

(columns 2 and 3) are listed in column 6. These values agree reasonably well with the values calculated based on the synthesis. Columns 7-11 contain composition data based on differential scanning calorimetry (DSC) measurements. As noted previously, these materials exhibited two hard segment T_g 's that were ascribed to the hard (phase 1) and soft (phase 2) segment-rich phases respectively. The weight fraction and composition values for these phases were determined from the positions and magnitude of the glass transitions. The composition and weight fraction values determined by the IR and DSC methods are in agreement for sample 4T10 but exhibit some discrepancies for the other two samples. For both samples 4T4 and 6T4 the IR fractionation data indicate a more even proportion of the hard and soft segment rich material. This behavior would be expected to be accompanied by a decrease in the hard segment content of the soluble fraction as is observed and an increase in the hard segment content of the insoluble material which is not observed. For both samples 4T4 and 6T4 the insoluble and phase 2 portions of the material have the same composition (17 and 15 percent hard segment respectively) but different weight fraction values. Thus for sample 4T4 the IR data indicate that 44% of the sample has an average weight fraction of 17% hard segment content while the DSC data indicate that 62% of the sample has an average weight fraction of 17%.

Careful consideration reveals that this result is only possible if the lowest hard segment content species in the sample are not included in the insoluble portion of the sample following the fractionation in DMF. This would not be unexpected since unreacted, low molecular weight, soft segment polyol is likely to be soluble under the fractionation conditions. Thus, the fractionation takes place on some combined basis of composition and molecular weight. If fractionation took place solely on the basis of composition, the compositions of the soluble and insoluble portions would give rise to at least as broad a distribution as the phase composition based on the DSC measurements. This fact

is important for modelling considerations because all of the models assume that fractionation takes place solely on the basis of composition.

The final three columns in Table 1 provide \bar{M}_w , \bar{M}_n and \bar{M}_w/\bar{M}_n values for the three samples based on GPC data and a co-(polyethyleneoxide-polyethyleneglycol) calibration curve²⁰. Thus, these values are only relative and it is not even clear whether the true values are generally lower or higher than the values shown in Table 1^{16,25}. Obtaining more accurate molecular weight values is difficult²⁵, and the relative nature of the measurement should not appreciably affect the \bar{M}_w/\bar{M}_n values. The large \bar{M}_w/\bar{M}_n values do clearly indicate the presence of non-ideal effects since under ideal conditions $\bar{M}_w/\bar{M}_n \leq 2^1$.

Table 2 contains the results of simulations performed using the single-phase ideal reaction model. In these simulations all of the model parameters were fixed except for the block or segmental degree of polymerization (BD_p). The value of A, the moles of isocyanate was determined by the average composition. Note that the value of A does not correspond to the synthesis value (Table 1) because non-stoichiometric conditions cannot be modelled with the SPI and because the 'target' average composition value was taken as the value calculated from the fractionation data (Table 1 column 5) and not the synthesis value. The values for the diisocyanate reactivity ratio, u , (not shown) were 12 and 6 for 2, 4 TDI and 2, 6 TDI respectively⁵. The soft segment molecular weight distribution was modelled by a Schulz distribution with $\bar{M}_n = 2200$ and $\bar{M}_w/\bar{M}_n = 1.5^{23}$. Since 'lop-off' effects¹ were not considered to be likely because the polymerization was done in bulk, the only variable parameter was BD_p . As BD_p increased, the molecular weights increased while the composition distribution became less broad.

For each sample, the results of three different simulations are reported in Table 2. The sample designations, for example 4T4-C, 4T4- \bar{M}_n , and 4T4- \bar{M}_w , indicate whether the BD_p value was adjusted to match the experimental composition

(from fractionation data), \bar{M}_n , or \bar{M}_w data. The resulting composition distributions, for sample 4T4, can be seen in Figure 1 which shows that the simulations exhibit similar but distinct composition distributions. (As discussed previously¹⁻³ Figure 1 is a plot of the intermediate weight fraction versus composition. The x-axis is the cumulative weight fraction of chains summed in ascending order of hard segment composition. As x increases, the chains within an x interval possess a higher average hard segment content than chains in previous x intervals. The y axis is a measure of this change and is termed the specific hard segment weight fraction.) Obviously, the SPI model cannot even approximately match the composition and molecular weight values simultaneously. In particular, as noted previously the model cannot produce \bar{M}_w/\bar{M}_n values greater than 2 and thus the experimental values $\bar{M}_w/\bar{M}_n \geq 4$ are a strong indication of non-ideal reaction conditions. This is an important point because the model can be used to simulate the composition data and the resulting molecular weight values, especially \bar{M}_n , are not that inadequate considering the inaccuracies in and the relative nature of the molecular weight measurements. It should also be noted that the composition data based on the DSC measurements could serve as an alternative to the fractionation data as a basis for the composition modelling. This suggestion has merit in that although the model simulates a fractionation procedure, it appears that the experimental fractionation occurred at least partly on the basis of molecular weight and the resulting values indicate a narrower composition distribution than would be expected if the fractionation, as the model assumes, occurred based solely on composition. Thus, the phase compositions which in two cases indicates a broader composition distribution might serve as better target values. Nevertheless, when these values were used as target values (data not shown) the resulting match of \bar{M}_n and \bar{M}_w was not significantly better than the results presented in Table 2. Finally, it is important to note that the composition matched data do indicate that the primary

effect of whatever non-ideality is occurring during the polymerization is to limit the molecular weight of the system. In other words the observed broad composition distribution is not unexpected (or is of 'natural' origin¹) in light of the low molecular weight values.

The results of simulations performed using the two-phase ideal reaction model are displayed in Table 3. Since the TPI model contains additional parameters, namely the composition of the phases (the amount of MDI and PBD in the MDI and PBD rich phases respectively) and the block degree of polymerization of each phase, the modelling does not proceed in exactly the same fashion as for the SPI model. To begin with however, the values of μ and the soft segment molecular weight parameters were fixed as described previously. Also, the value of A was again determined by the average composition of the sample based on the experimental composition data (note that both the DSC and the fractionation based composition data yield similar average compositions). At this point, two different approaches were used. If the DSC based 'phase' compositions were used as targets, the values of the fraction of MDI in the MDI rich phase and the fraction of PBD in the PBD rich phase could be calculated since the model does not allow for non-stoichiometric conditions. This condition was termed phase-matched and is indicated by a -P in the sample designation. When this approach was used it was not possible to achieve matching fractionation composition data. As expected, based on the previous discussion, the simulated fractionation composition data always indicated a broader composition distribution than the experimental data. Alternatively, matched fractionation composition data (-C sample designation) could be achieved but the simulated phase composition values indicated a composition distribution that was too narrow.

Several other points should be made with regard to the modelling procedure using the TPI model. First of all for composition matched samples, the effects of varying the MDI/PBD fractions and molecular weight and BD_{p1} and BD_{p2} on the

composition data are not independent. Thus a trial and error procedure was used. Similarly for the phase match simulations, the matching of the \bar{M}_n and \bar{M}_w values involved a trial and error procedure with BD_{p1} and BD_{p2} . Because the phase-matched simulations only involved two varying parameters (BD_{p1} and 2) and because of the problems involved with the relationship of the fractionation simulation and experimental data, the phase-matched approach was favored and Table 3 only includes composition matched results for one sample (4T4) for comparison.

The most significant data in Table 3 are the molecular weight values. By proper manipulation of BD_{p1} and BD_{p2} it was possible under either phase-matched or composition-matched conditions to achieve simultaneously good matching with the \bar{M}_n and \bar{M}_w values, at least for samples 4T4 and 6T4. For sample 4T10 the inability to produce matched molecular weight values is a result of the definition of the degree of polymerization in terms of segments and not monomers. This assumption is particularly bad in the case of sample 4T10 because the average hard segment contains 21 monomer units whereas for samples 4T4 and 6T4 the average hard segment contains only 7 or 8 monomers. Thus a very low BD_p is needed to obtain the experimental \bar{M}_n value (note the BD_{p2} value of 1.05 for sample 4T10). In fact for all 3 samples the BD_{p2} values are low enough that the error involved in using segments instead of monomers is probably appreciable and even better results might be obtained if the model was modified.

Table 3 also contains \bar{M}_w/\bar{M}_n values for the simulated sol and gel (insoluble) fractions. These values reveal that the soft segment rich fraction (insol) has a lower molecular weight and a narrower molecular weight distribution. The fact that \bar{M}_w/\bar{M}_n for the soluble fraction is much greater than 2 is a clear indication that the simulated soluble and insoluble fractions do not correspond directly to the simulated hard and soft segment rich phases (phase 1

and phase 2) even for sample 4T10. IF they did $\bar{M}_w/\bar{M}_n \approx 2$ since by definition of the model $\bar{M}_w/\bar{M}_n \approx 2$ in each of the phases. A plausible scenario based on the data would be that almost all of the hard segment rich phase (phase 1) is included in the soluble fraction along with some very low molecular weight, hard segment rich (probably single hard segments ($BD_p=1$)) material from the soft segment rich phase.

The results of the modelling using the TPI model support several conclusions regarding the polymerization of the PBD polyurethanes. First, considering the experimental accuracy, the excellent agreement between the simulated and experimental composition and molecular weight values using the TPI model strongly supports the hypothesis of MacKnight and coworkers that phase separation occurred near the beginning of the reaction. The major effect of this phase separation process appears to be the limitation of the molecular weight especially in the soft segment rich phase (note the low values of BD_p2). The low molecular weight would be expected due to stoichiometric imbalances in each phase following phase separation²⁴ and as noted previously would also lead to the observed broad composition distribution. The broad molecular weight distributions (high \bar{M}_w/\bar{M}_n) values arise from the large difference between BD_{p1} and BD_{p2} . Based on the polymerization scenario suggested by MacKnight and coworkers it appears that little butanediol diffused into the PBD rich regions and thus the PBD rich phase is primarily the low molecular weight product of the first (prepolymer) step of the reaction. The high molecular weight portions of the soluble fractions in Table 3 could be considered to have been the results of reactions of long hard segments with prepolymer segments at the interface of the hard segment rich regions.

The final model that was used to simulate the experimental composition and molecular weight data of the polybutadiene polyurethanes was the simple sinking

pool model. The results obtained with this model are shown in Table 4. However, before discussing these results the modelling procedure will be briefly described. The molar excess of isocyanate to chain extender (A-B) (note all ratios are based on one mole of polyol) was kept constant at the synthesis value but the absolute values of A and B were again adjusted to match the average composition calculated from the fractionation data. The soft segment molecular weight characteristics were the same as noted above and μ values were unnecessary. It was then possible to manipulate the D_p , SAF and NSA or the D_p and RCF parameters to obtain good matches to the fractionation composition and \bar{M}_n values. Alternatively, the composition and \bar{M}_w values could be matched but it was not possible to simultaneously match the \bar{M}_n and \bar{M}_w data. Varying the SAF or RCF gave rise to similar effects and there are many possible combinations of these two parameters that give similar composition and molecular weight data. Table 4 displays the results of three simulations each for samples 4T4 and 4T10. In the first simulation of each set ($-\bar{M}_n1$) self-affinity is not used and only RCF along with D_p was varied. The effects of varying the parameters are not independent but varying D_p mainly influences the molecular weight values while changing RCF primarily affects the composition data. In the second simulation of each set ($-\bar{M}_n2$), RCF is set at 1.0 (ideal value) and the self-affinity factor (SAF) is varied with NSA = 10 and D_p equal to the same value as the \bar{M}_n1 simulation. A third simulation (\bar{M}_n3) was performed with NSA = 1. Both simulations gave rise to similar molecular weight and composition data but as expected as NSA decreases the value of SAF necessary to achieve given composition values also decreases. It would also be possible to achieve the given values of \bar{M}_n and composition by varying both RCF and SAF.

Based on the results of the modelling with the TPI model one might expect similar or even better results to be obtained with the simple sinking pool model for several reasons. First, the SSP model defines the degree of polymerization

in terms of monomers instead of segments which should eliminate the problems noted previously. Second, the model allows for non-stoichiometric conditions, which almost undoubtedly exist during the actual polymerization in the individual phases and probably are the major factor limiting molecular weight. Third, the model allows for unequal reactivity of the chain extender and the polyol; a situation that is not unlikely in a bulk polymerization due to the higher mobility of the chain extender. However, despite those advantages the results of the simulations using the SSP model shown in Table 4 indicate that the simulated data, primarily the \bar{M}_w/\bar{M}_n values, do not match the experimental data.

This inadequacy of the model is a result of the manner in which the phase separation process is modelled. Although the self-affinity concept is appealing in that it is more flexible than the partitioning method used in the TPI model it generally does not produce very broad (>3) \bar{M}_w/\bar{M}_n values. This is because although the probability of reacting with a given monomer can be influenced, changing the self-affinity in the model has no effect on the D_p of any given chain. In fact, self-affinity and unequal reactivity effects should lead to deviations from a most probable D_p distribution; however there is no simple method for calculating what the distribution should be^{3,18}. It should be possible using a Monte Carlo method similar to that of Chaumont et al.²⁶ to calculate the D_p distribution. Higher \bar{M}_w/\bar{M}_n values can be achieved if all of the chains are assumed to start polymerizing at the same instant because of the accentuated depletion effects³, but \bar{M}_w/\bar{M}_n values greater than 5 still are not normally obtained.

Several other observations should be noted regarding the data in Table 4. First it is interesting that good agreement with the composition and \bar{M}_n data can be achieved for sample 6T4 without the use of any non-ideal effects ($SAF = 0$, $RCF = 1.0$). This is surprising because similar results could not be obtained using the SPI model; the difference can be related to the way the degree of

polymerization is defined in the two models. Note that to match the composition data for sample 6T4 using the SPI model a higher BD_p value was needed than that necessary to match the \bar{M}_n data (Table 2). Apparently for sample 6T4, that difference is balanced out in the SSP model when the D_p in terms of monomers is used. The effect of changing the way the degree of polymerization is defined can also be noted in the D_p values for the simulations of sample 4T10 using the SPI and SSP models. With the SPI model, BD_p for sample 4T10 was normally lower than the BD_p values for the other samples while in the SSP model the D_p values are higher. Finally, the effect can also be seen in the molecular weight data for the soluble and insoluble fractions. In the SPI and TPI models, the \bar{M}_n and \bar{M}_w values for the sol fractions were generally the same or higher than the values for the insoluble fraction. However, the situation is reversed for the SSP model because there are many more low molecular weight high hard segment content species. In the SPI and TPI models only chains with a BD_p of 1 and possibly 3 would fall into that category while in the SSP model pure hard segments with D_p 's of 1 to about 10 would qualify.

A comparison of the three models can be made for sample 4T4 using Figures 2 and 3. Figure 2 is a plot of the composition distributions for sample 4T4 using the SPI model (4T4-C, Table 2), the TPI model (phase-matched 4T4-P and composition matched 4T4-C2 Table 3) and the SSP model (4T4- \bar{M}_n 2 Table 4). The various composition distributions are not that dissimilar which is not surprising because all of the models provide the same fractionation composition data except the phase-matched TPI simulation which shows the greatest deviation from the other curves. Note that the phase-matched TPI data, which as discussed previously are probably more accurate, exhibit a composition distribution with two plateaus characteristic of a material that underwent phase separation during polymerization. The molecular weight distributions (Figure 3) are markedly different and provide, as noted previously, a better basis for distinguishing

between the three models. (As expected the distributions calculated using the TPI model are similar. However, these two simulated samples are easily distinguished on the basis of their composition distributions (Figure 2)). Similar conclusions can be drawn regarding sample 4T10 (Figures 4 and 5) however the differences between the models are larger because of the greater effect of changing the way the degree of polymerization is defined and the broader experimental molecular weight ($\bar{M}_w/\bar{M}_n \approx 7$) and composition distributions of this sample.

Summary and Conclusions

Several conclusions can be drawn from the results of these attempts to model the experimental composition and molecular data of the polybutadiene polyurethanes previously studied by MacKnight and coworkers. First the fact that the data can be best simulated by the two-phase ideal reaction model supports the assertion made by MacKnight and coworkers that these samples underwent phase separation during polymerization. Furthermore, it appears that the major effect of the phase separation was to limit the molecular weight of the soft segment rich phase in particular, probably due to large stoichiometric imbalances of the reactants in the two phases. This low molecular weight in turn produced the expected and observed broad composition distribution. The phase separation process also led to a broad molecular weight distribution which is probably due to the ability of the system to have different average degrees of polymerization in the two phases.

With regard to the models themselves it is apparent that they have several shortcomings that could be improved for modelling actual experimental data. The fractionation procedure should be modified so that it could simulate molecular weight effects. The SPI and TPI models are not as accurate at low molecular weight because of the way they define the degree of polymerization, while the

SSP model cannot give rise to large \bar{M}_w/\bar{M}_n values. A superior model might be obtained by combining some of the features of the TPI and SSP model. A different modelling approach which does not prefix the D_p for a given chain should also be investigated. Also, the simulation of crosslinking would be beneficial; indeed allophonate crosslinking is suspected to exist in the PBD polyurethanes²¹ and may partially account for their broad \bar{M}_w/\bar{M}_n values and solubility behavior. Numerous other improvements could also be made; however most of the improvements increase the model complexity. More complex models in general require more experimental data to accurately distinguish between models or determine values of model parameters. For example, in the present study, the accuracy of the models could be further tested if molecular weight values for the soluble and insoluble fractions and/or data on the hard segment length distributions were available. Obviously, additional experimental and theoretical work is needed to obtain a better understanding of the polyurethane polymerization process under various conditions.

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TABLE 1

Composition and Molecular Weight Data
For Polybutadiene Polyurethanes

Sample	Weight Fraction		Hard Segment		Weight Fraction		Hard Segment		\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
	sol.	insol.	sol.	insol. calc.	Phase 1	Phase 2	Phase 1	Phase 2 Calc.			
4T4-4.2/3/1-31.3	.56	.44	41.7	17.0 30.8	.38	.62	53.0	17.0 30.7	28,800	7,300	3.9
4T10-10.5/9/1-54.5	.80	.20	67.5	10.5 56.1	.80	.20	67.5	10.5 56.1	32,300	4,400	7.3
6T4-4.2/3/1-31.3	.54	.46	35.0	15.0 25.8	.38	.62	43.0	15.0 25.6	18,300	3,000	6.1

TABLE 2

Results of Simulations Using the
Single-Phase Ideal Reaction Model

Sample	BDp	A	Composition			Molecular Weights							
			Avg.	Insol.		Sol.	Overall			Insol.			Sol.
				\bar{M}_w	\bar{M}_n		\bar{M}_w/\bar{M}_n	\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w	\bar{M}_n	
4T4-C	4.0	4.0	30.8	17.0	41.7	6,200	11,600	1.9	6,400	11,300	6,000	12,000	
4T4-M _n	4.75	4.0	30.7	18.5	40.3	7,400	13,900	1.9	7,500	13,400	7,200	14,300	
4T4-M _w	9.7	4.0	30.7	22.6	37.2	14,900	28,800	1.9	14,800	27,900	14,900	29,600	
4T10-C	2.15	10.9	56.2	11.1	67.5	5,300	9,700	1.8	3,200	5,600	6,300	10,800	
4T10-M _n	1.8	10.9	55.9	5.9	68.6	4,400	8,150	1.8	2,700	4,400	5,300	9,100	
4T10-M _w	6.9	10.9	56.0	34.2	61.4	16,900	32,700	1.9	10,400	20,600	20,000	35,700	
6T4-C	4.5	3.2	25.7	14.9	34.9	6,100	12,500	1.9	6,900	12,000	6,100	12,500	
6T4-M _n	2.1	3.2	25.7	7.3	41.4	3,100	5,600	1.8	3,400	5,600	2,700	5,500	
6T4-M _w	6.7	3.2	25.7	17.3	32.9	9,700	18,800	1.9	10,100	18,100	9,400	19,300	

TABLE 3

Results of Simulations Using the
Two-Phase Ideal Reaction Model

Sample	A	BD _{p1} , BD _{p2}	Fractions* MDI, PBD	Composition				Overall				Molecular Weights			
				Phase 1		Phase 2		\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w	Sol.
				Avg.	Insol.	Sol.	Avg.								
4T4-P	3.96	13.0, 3.8	.62, .745	53.0	16.8	30.8	11.7	45.9	7,300	28,700	3.9	6,400	10,500	8,200	43,300
4T4-C ₁	3.96	13.0, 3.8	.56, .62	40.2	22.9	30.7	16.8	41.7	8,100	26,200	3.2	6,700	11,300	9,600	38,200
4T4-C ₂	4.0	15.0, 3.4	.55, .62	39.7	23.8	30.8	16.9	41.9	7,500	28,700	3.8	6,200	10,800	9,000	43,200
4T10-P	11.0	6.0, 1.05	.97, .315	64.5	7.4	56.0	9.9	67.7	5,900	31,200	5.2	2,700	62,600	8,300	37,700
6T4-P	3.25	11.3, 1.55	.61, .70	43.1	15.1	25.9	5.2	44.0	3,100	19,300	6.3	2,900	4,400	3,100	33,000

* Fraction of total MDI in MDI-rich phase (Phase 1) and fraction of total PBD in PBD-rich phase (Phase 2).

Results of Simulations Using the Simple Sinking Pool Model

Sample	A/B	D _p	RCF	SAF	NSA	Composition			Molecular Weights						
						Avg.	Insol.	Sol.	Overall			Insol.			Sol.
									\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{M}_n	\bar{M}_w	\bar{M}_n	
4T4-M _n 1	4.08/2.88	19	1.72	0	-	30.8	17.3	41.5	7,300	16,800	2.3	11,800	20,200	5,700	14,100
4T4-M _n 2	4.07/2.87	19	1.0	.21	10	30.6	17.1	41.3	7,500	16,100	2.1	11,500	18,600	5,800	14,200
4T4-M _n 3	4.07/2.87	19	1.0	.11	1	30.7	17.4	41.3	7,400	15,400	2.1	11,000	17,300	5,800	13,850
4T10-M _n 1	11.1/9.6	20	6.0	0	-	56.0	11.0	67.5	4,500	13,300	3.0	15,300	28,800	3,800	9,400
4T10-M _n 2	11.1/9.6	20	1.0	100	10	56.0	10.7	67.5	4,500	12,300	2.7	13,300	31,000	3,800	7,500
4T10-M _n 3	11.1/9.6	20	1.0	4.2	1	55.9	10.4	67.5	4,500	9,500	2.1	8,500	13,300	4,000	8,600
6T4	3.35/2.25	6.8	1.0	0	-	25.8	38.5	11.6	3,100	7,500	2.4	5,800	8,800	2,300	6,300

Figure Captions

- Figure 1. Specific hard segment weight fraction versus cumulative weight fraction for the Single-Phase Ideal Reaction Model samples 4T4-C, 4T4-M_n, and 4T4-M_w
- Figure 2. Specific hard segment weight fraction versus cumulative weight fraction for samples 4T4-C (SPI), 4T4-P (TPI), 4T4-C2 (TPI), and 4T4-M_n2 (SSP)
- Figure 3. Molecular weight distributions for samples 4T4-C (SPI), 4T4-P (TPI), 4T4-C2 (TPI), and 4T4-M_n2 (SSP)
- Figure 4. Specific hard segment weight fraction versus cumulative weight fraction for samples 4T10-C (SPI), 4T10-P (TPI), and 4T10-M_n2 (SSP)
- Figure 5. Molecular weight distributions for samples 4T10-C (SPI), 4T10-P (TPI), and 4T10-M_n2 (SSP)

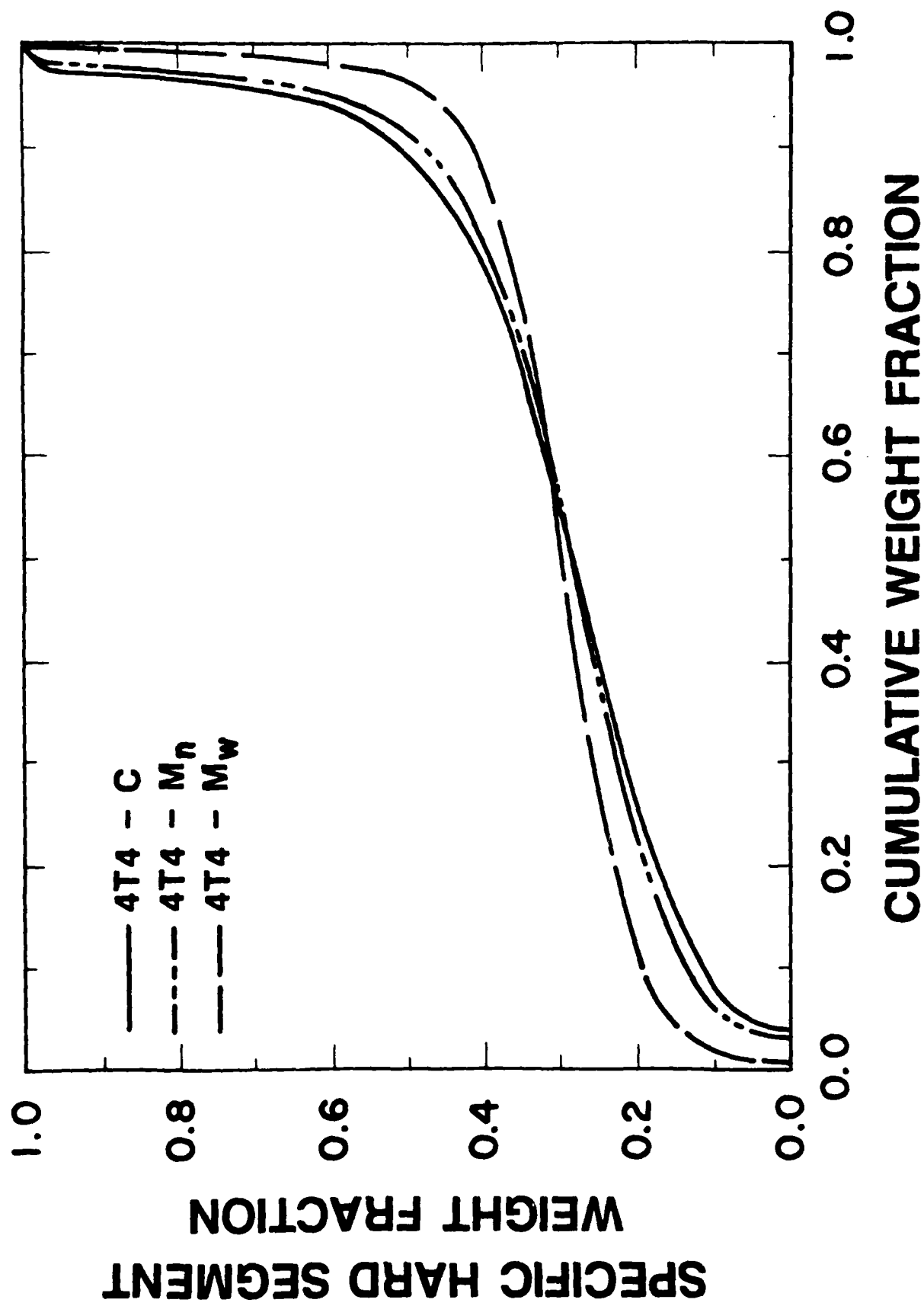


Figure 1

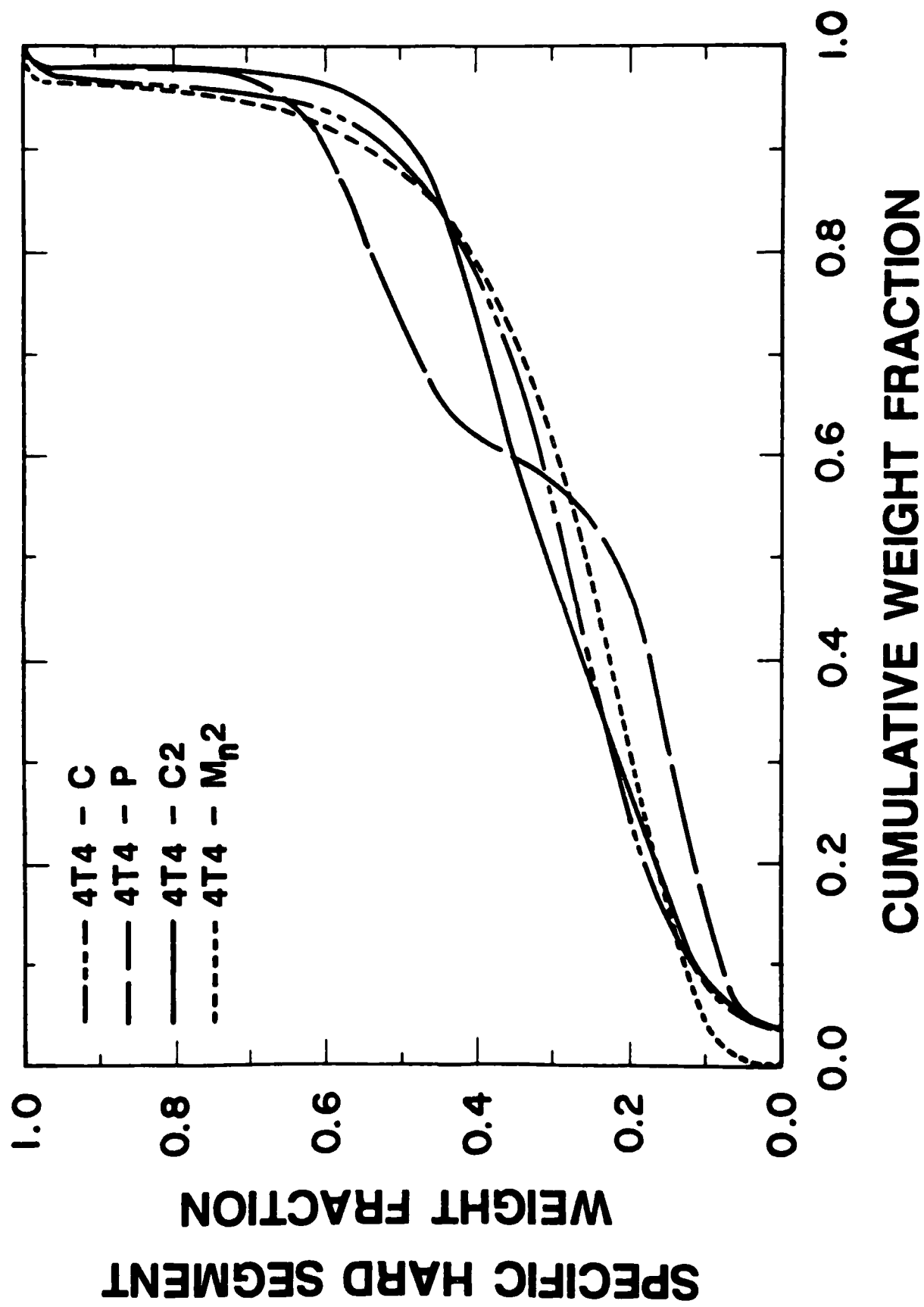


Figure 2

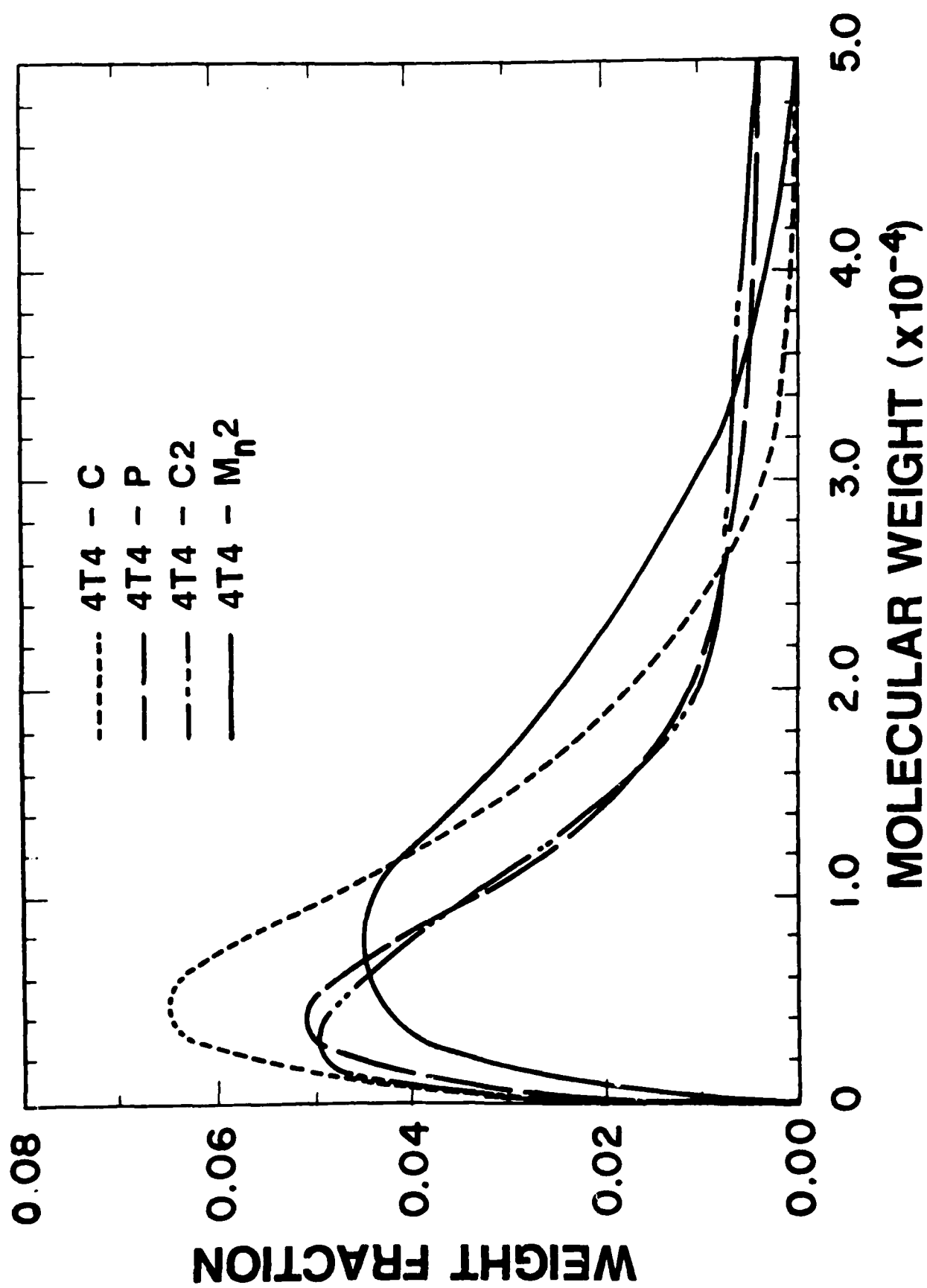


Figure 3

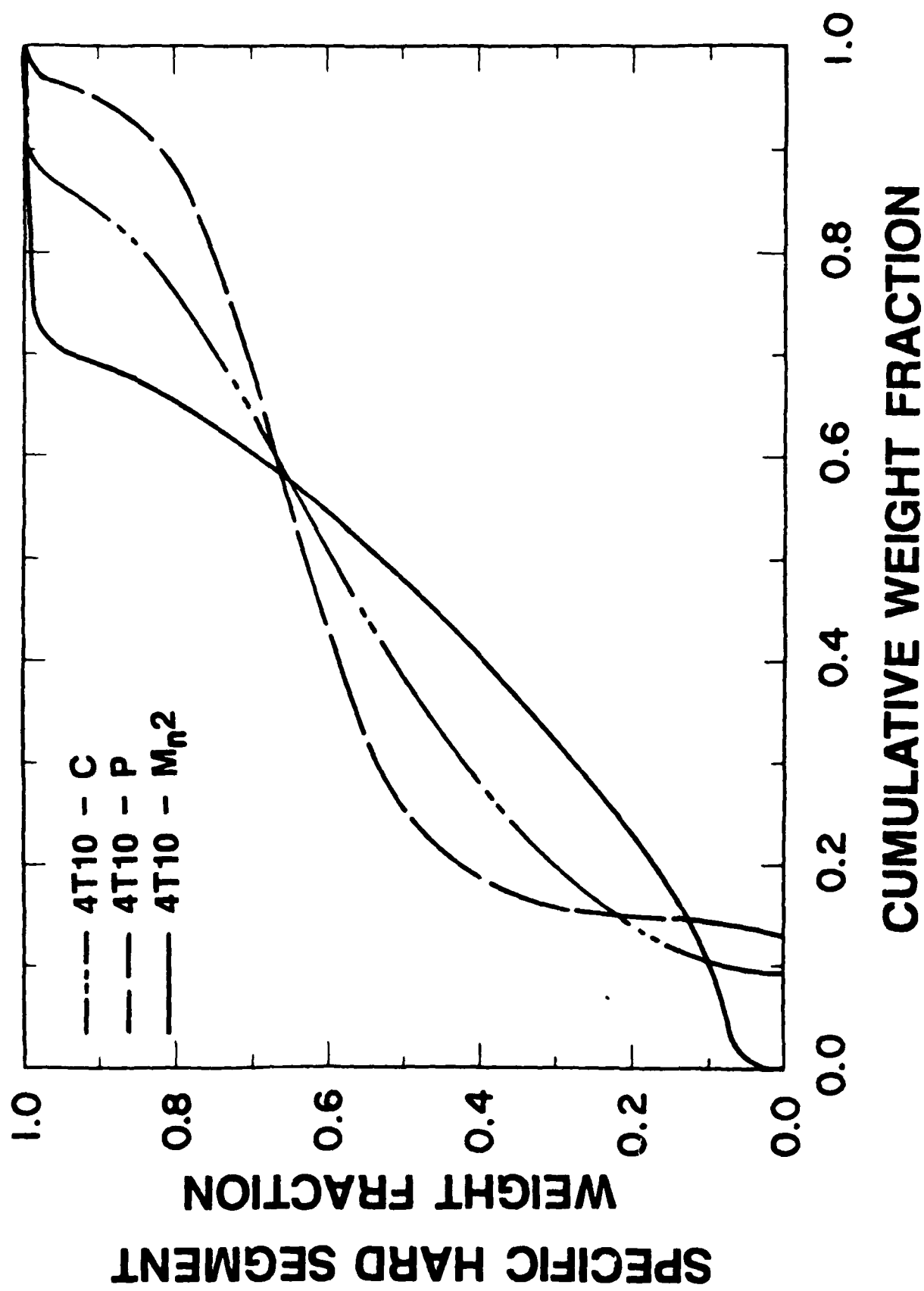


Figure 4

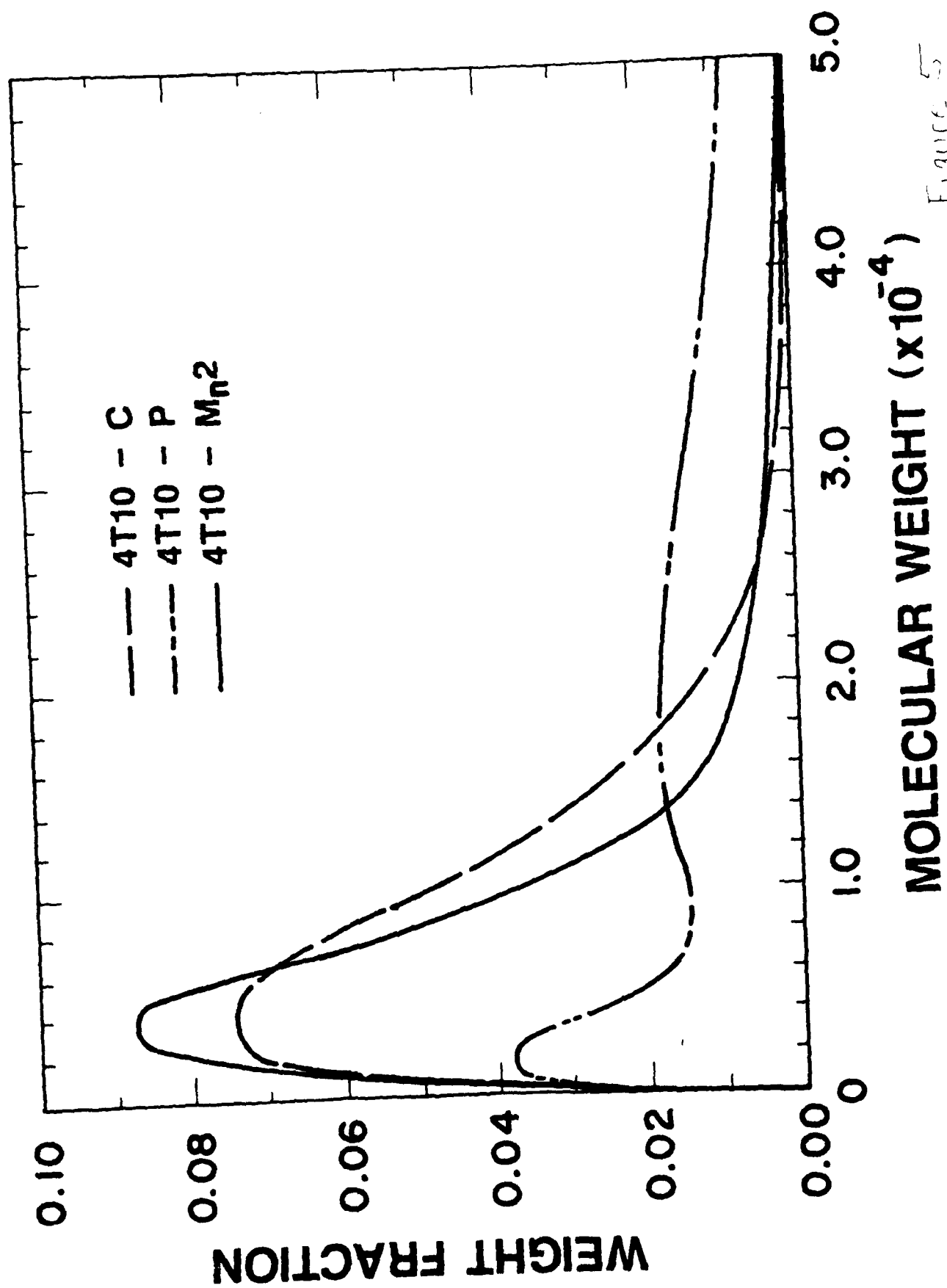


Figure 5

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